THE FURTHER EXTENSION OF THE ULTRA-VIOLET SPECTRUM AND THE PROGRESSION WITH ATOMIC NUMBER OF THE SPECTRA OF LIGHT ELEMENTS

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Read before the Academy April 26, 1920

The chief purpose of this investigation, outlined and begun in 1916[1] and briefly reported upon last year,[2] has been to explore in the extreme ultra-violet the radiations which can be emitted by the second ring or shell of electrons in the atoms of atomic number from 2 to 13 (helium to aluminium).[3]

The results obtained to date may be very briefly summarized as follows:[3]

1. The ultra-violet spectrum has been photographed and its wave-lengths determined down to $\lambda = 136.6$ Ångstroms in the case of aluminium and down to $\lambda = 149.5$ Ångstroms in the case of copper. There is thus a gap represented by a factor of but 10 between the shortest measured ultra-violet waves and the longest X-rays measured by the method of crystal-spectrometry which stops at 13.3 Ångstroms. *Fortunately, however, in the ultra-violet region, which has been already opened up and explored, the most interesting and the most important of the hitherto inaccessible radiations are found;*—thus

2. The L_α lines of Al, Mg, and Na have been photographed and located at 144.3 Å, 232.2 Å, and 372.2 Å, respectively. These wave-lengths are all fairly accurately on the Mosely line connecting L_α frequencies and atomic number (see fig. 1). *It has thus been definitely proved that the L series continues with its main characteristics unchanged throughout the whole range of atomic numbers from Ur (92) to Ne (10).* The linear progression thus revealed clear down to neon could be very roughly inferred from the beautiful measurements of Hjalmar,[4] which gave the K_α and K_β lines of the elements down to sodium. For the Kossel relation between the frequencies of the K and L series, namely, $K_\beta - K_\alpha = L_\alpha$, although known to be quite inexact, was presumably sufficiently near to the truth to enable *the order of magnitude* of the L_α wave-lengths to be predicted. Kossel has already made this use of Hjalmar's data.[5] His values of L_α computed for Al, Mg and Na in this way are actually about 20% too low.

3. It has been found that *the aluminium atom (atomic number 13) when excited by these condensed sparks in vacuo emits no radiations whatever of wave-length between 144.3 Å and about 1200 Å where its M spectrum,* that due to its three outer electrons, begins and extends with considerable complexity into the visible. *This shows that optical spectra are quite like*

X-ray spectra in that large gaps occur between the frequencies due to the electrons in successive rings or shells. If we could neglect the influence of the negative electrons upon one another we could compute the relative diameters of these shells, for they would be inversely proportional to the limiting frequencies, i.e., in this case in about the ratio 1 to 9; but such computations are of little value save as the roughest sort of indices. The chief lines below 2000 Å, due to the three outer electrons of the Al atom have the wave-lengths 1379.7 Å, 1384.5 Å, 1605.9 Å, 1612.0 Å, 1671.0 Å, 1854.7 Å and 1862.7 Å.

Magnesium shows a behavior quite like that of aluminium in that we find a complete blank between its L_α line at 232.2 Å and the lines due to its two outer electrons whose radiations begin on our plates on the short wave-length side at about 1700 Å. The chief radiations below 2000 Å, arising from these two outer electrons of the magnesium atom, have the wave-lengths 1735.2 Å, 1737.9 Å, 1751.0 Å, and 1753. 7 Å.

Also, *sodium*, quite consistently with the foregoing, is found to emit no radiations whatever between its L lines, the longest of which is at 376.5 Å and the lines due to its single M electron which have their convergence wave-length at 2412.63 Å, and reach their maximum intensity in the familiar sodium doublet at 5890 Å and 5896 Å.

4. Coming now to the group of atoms below neon, atomic number 10, the spectra due to the electrons in the incomplete second or L-ring in the case of these atoms are completely unpredictable from any theory that we now have but they have been experimentally obtained. For reasons which will appear they will not be considered in the order of atomic number.

a. The spectrum due to the six L-ring electrons of the oxygen atom (atomic number 8) begins upon our plates at about 230 Å and extends with much complexity and strength up to 834.0 Å where the strongest oxygen line, which will be arbitrarily called its L_α line, is found. Above 834.0 Å the oxygen lines are few in number and relatively faint.

Since the K_α line of O can be computed with much certainty to be at 23.68 Å, the ratio of the K frequency to the L frequency for the oxygen atom is about 35. It will be recalled that this ratio is only about 7 in the case of atoms of high atomic number and that it slowly increases with decreasing atomic number, reaching the values 17.2, 23.4 and 31.1 in the cases of Al, Mg, and Na, respectively (see above). The strongest of the oxygen lines have the following wave-lengths: 321.2, 374.3, 507.8, 525.7, 554.2, 599.5, 610.1, 616.7, 625.2, 629.6, 644.0, 703.1, 718.5 and 834.0.

The oxygen lines have been identified because they appear as impurities in all easily oxidizable metals, NrLi, Mg, Al, Zn, Fe, etc., The key to the oxygen spectrum was furnished by the discovery that chemically pure aluminium and magnesium showed the extraordinary property

of having identical spectra in all particulars between 1000 Å and 235 Å, while showing altogether distinct characteristic spectra between 1700 Å and 6000 Å, a behavior which could only mean that they themselves had no lines in the region, between 235 Å and 1000 Å, all of the observed lines being those of the common impurity oxygen—an interpretation supported by the fact that the well known oxygen lines of the visible region were also found in both spectra. It was with the aid of this discovery and the careful comparison of the spectra of otherwise pure metals, or of metals containing known impurities that the origins of practically all of the hundreds, even thousands, of new lines have been established with but very little uncertainty.

b. The spectrum due to the 4 L-ring electrons of the *carbon* atom begins upon our plates at 360.5 Å and extends with much complexity and strength up to 1335.0 Å where its strongest line, which, in harmony with the foregoing convention will be called its $L_\alpha{}^6$ line is found. Above 1335.0 Å, the carbon lines are widely scattered and relatively weak. Since the K line of carbon is accurately computed to be at 44.4 Å, the ratio of the K to the L frequency in carbon is about 30.

It is interesting that practically the whole group of lines which Lyman obtained from his *condensed discharge in helium*[7] are due to carbon, oxygen, nitrogen and hydrogen. Thus those whose wave-lengths he gives as 599.0, 643.7, 702.9, 718.2, 796.8 and 834.1 are all due to oxygen; those whose wave-lengths he gives as 904.6, 977.2, 1010.6, 1037.0, 1175.9 and 1247.9 are due to carbon; those whose wave-lengths he gives as 916.7, 991.1 and 1085.5 are due to nitrogen; while those whose wave-lengths he gives as 972.7, 1026.0, 1216.0, are due to hydrogen.

c. The spectrum due to the 5 L-ring electrons of the nitrogen atom (atomic number 7) was obtained by using Al electrodes with ammonium nitrate in their cores and observing the new lines which were not due to aluminium, oxygen or hydrogen. Before this experiment was tried, it was predicted that the L_α line of nitrogen would have to lie between the L_α line of oxygen and that of carbon. It was found that the spectrum due to the nitrogen atom was very simple, beginning on our plates on the short wave-length side at 685.6 Å and *reaching a maximum in the line of wave-length 1085.3 Å, precisely as predicted.* This 1085.3 line is taken, in accordance with the foregoing convention, as the L_α line of the nitrogen atom. The only other strong lines which we have obtained which are due to this atom have the following wave-lengths: 685.6, 916.2, 991.1. The pair of nitrogen lines found by Lyman at 1492.8 and 1494.8 appear upon our plates, but they are very faint in comparison with the foregoing lines, the nitrogen spectrum thus showing a behavior quite like that due to the atoms of oxygen and carbon. Since the K_α line of nitrogen is at 31.2 Å, the ration of the K_α to the L_α frequency is 34.8.

d. In the case of *fluorine* a strong line has been found through the use of sodium fluoride at 657.2 Å. This is in about the position predicted by the foregoing mode of approach for its L_α line. Another strong fluorine line appears at 607.2 Å. These are the only lines thus far definitely identifiable as coming from the 7 L- ing electrons of the fluorine atom. The longer of these wave-lengths is taken as the L_α line of fluorine. Fluorine probably has, however, other lines of shorter wave-lengths but of such intensity that we have not yet been able to obtain them.

e. The spectrum, due to the 3 L-ring electrons of boron (atomic number 5) is especially interesting because of its simplicity. It contains less than 10 strong lines all told. It begins on the short wave-length side at 676.8 Å and has only the following strong lines: 676.8, 760.0, 1624.4, the two doublets at 2164.2, 2166.2 and 2496.9, 2497.8 and the single spark-line near the visible at 3451.5. According to the foregoing convention, its L_α line should be the doublet at 2497 Å. Since the K_α line of boron is at 67.2 Å, the ratio of the K_α to the L_α frequency in boron is about 37.

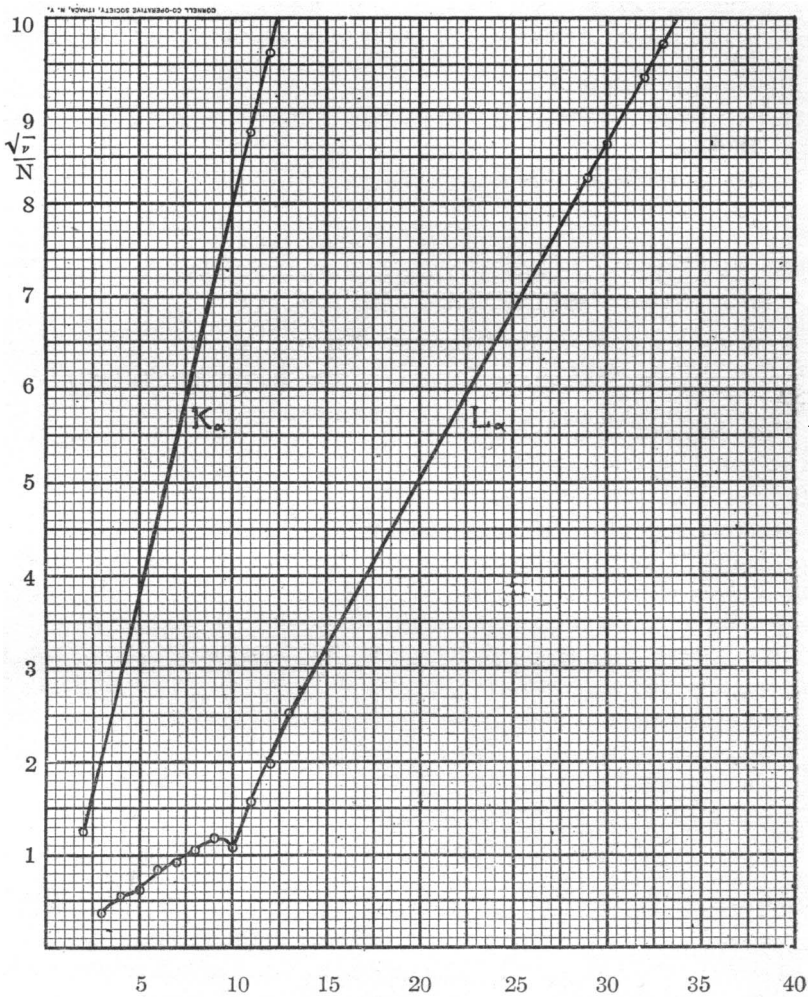
f. The spectrum due to the 2 L-ring electrons of *beryllium* begins on the short wave-length side, according to all the data available up to date, at 2175 Å and reaches its maximum, its L_α doublet, at 3130.6 and 3131.2. The entire absence upon our plates of any lines whatever due to beryllium between 230 Å and 2100 Å is a conspicuous illustration of the wide gaps in spectra obtained with ordinary gratings in or near the visible region.

g. Similiarly the present experiments with *lithium* (atomic number 3) reveal no lines whatever between the shortest wave-lengths measurable on the plates used in the case of lithium and the familiar series due to its single L-ring electron whose L_α line is at 6708 Å and whose convergence wave-length is at 2299 Å.

5. The graph of the L_α lines of the elements from lithium up is shown in the accompanying figure, along with the corresponding graph for the K_α lines from helium up taken from the work of others. *The only point on the L_α graph which has not been directly observed is that corresponding to neon which has been inserted from the resonance potential of that gas.*

It is to be observed that the method here employed gives, as I think, the characteristic spectra of the *atoms* of each element, not of the molecules. If it were possible to work with the *atomic gas* of each element, the L_α lines given herewith would be the *resonance* potentials of these atoms.

The progression thus revealed in these optical spectra is exceedingly interesting and simple, and very like that exhibited by X-ray spectra. The reason it has not been observed before is clearly because hitherto only the upper ends of these optical spectra have been observable, so that the unfolding of simple relationships between spectra and atomic number had to await the development of an ultra-violet technique.



L_α lines of Li, Be, B, C, N, O, F, Ne, Na, Mg and Al

A glance at the figure shows that we now have the complete outline of all of the types of radiations which are emitted by atoms of small atomic number. It remains only to fill in the details of their K_α and L_α spectra. One interesting fact which appears from a glance at the whole series of spectra of elements from hydrogen to neon is that atoms of odd ordinal all appear to have simple, few-lined spectra, while those of even ordinal number have much more complex spectra.

[1] *Physic. Rev.*, **10**, 1917 (205).
[2] *Astroph. J.* **52**, 1920 (47).

[3] A detailed paper giving the full spectra of the light atoms with photographs will soon be published in the *Astrophysical Journal* in collaboration with Mr. I. S. Bowen.

[4] *Zeit. Physik*, **1**, 1920 (439).

[5] *Ibid.*, **2**, 1920 (470).

[6] This convention is more logical than that used in a former paper (cit.[2]) in naming the L_α line.

[7] *Astroph. J.*, **43**, 1916 (102).

THE AVERAGE OF AN ANALYTIC FUNCTIONAL AND THE BROWNIAN MOVEMENT

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Communicated by A. G. Webster, March 22, 1921

The simplest example of an average is the arithmetical mean. The arithmetical mean of a number of quantities is their sum, divided by their number. If a result is due to a number of causes whose contribution to the result is simply additive, then the result will remain unchanged if for each of these causes is substituted their mean.

Now, the causes contributing to an effect may be infinite in number and in this case the ordinary definition of the mean breaks down. In this case some sort of measure may be used to replace number, integration to replace summation, and the notion of mean reappears in a generalized form. For instance, the distance from one end of a rod to its center of gravity is the mean of its length with reference to its mass, and may be written in the form

$$\int l dm \div \int dm$$

where l stands for length and m for mass. It is to be noted that l is a function of m, and that the mean we are defining is the mean of a function. Furthermore, the quantity, here the mass, in terms of which the mean is taken, is a necessary part of its definition. We must assume, that is, a normal distribution of some quantity to begin with, in this case of mass.

The mean just discussed is not confined to functions of one variable; it admits of an obvious generalization to functions of several variables. Now, there is a very important generalization of the notion of a function of several variables: the function of a line. For example, the attraction of a charged wire on a unit charge in a given position depends on its shape. The length and area of a curve between two given ordinates depend on its shape. As a curve is essentially a function, these functions of lines may be regarded as functions of functions, and as such are known as functionals. Since a function is determined when its value is known for all arguments, a functional depends on an infinity of numerical determi-